

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : C08F 220/24, 226/06 G02B 1/04</p>	<p>A1</p>	<p>(11) International Publication Number: WO 92/18548 (43) International Publication Date: 29 October 1992 (29.10.92)</p>
<p>(21) International Application Number: PCT/US92/03128 (22) International Filing Date: 16 April 1992 (16.04.92) (30) Priority data: 687,385 18 April 1991 (18.04.91) US 786,130 31 October 1991 (31.10.91) US (71) Applicant: OPTICAL RESEARCH, INC. [US/US]; Materials Development Corporation, 6003-121 Chapel Hill Road, Raleigh, NC 27607 (US). (72) Inventor: CHEN, Richard, Y., S. ; 1021 Kinsdale Drive, Raleigh, NC 27615 (US). (74) Agents: MYERS, James, D. et al.; Bell, Seltzer, Park & Gibson, P.O. Drawer 34009, Charlotte, NC 28234 (US).</p>	<p>(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: NOVEL COMPOSITION FOR CONTACT LENSES (57) Abstract A hydrogel copolymer for making contact lenses comprises, by weight, about 5 to about 85 percent of α-methylene-N-methylpyrrolidone or glycerdyl methacrylate and mixtures thereof from about 5 to about 35 percent of N,N-dimethylacrylamide, from about 5 to about 60 percent of a polymerizable fluoromonomer, and from about 1 to about 15 percent of a polymerizable hydrophobic non-hydrolyzable silicone monomer. An initiator and a crosslinker are usually preferably also employed.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	RU	Russian Federation
CG	Congo	KP	Democratic People's Republic of Korea	SD	Sudan
CH	Switzerland	KR	Republic of Korea	SE	Sweden
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
DE	Germany	MC	Monaco	TC	Togo
DK	Denmark			US	United States of America

NOVEL COMPOSITION FOR CONTACT LENSES

Background of the Invention

5 This invention relates to contact lenses, and in particular to pliable or "soft" contact lens having an exceptional combination of oxygen permeability, strength, and resistance to protein and mucus deposits. There is a great need for a contact lens that has high oxygen permeability and wettability and resistance to protein and mucus deposits. These properties all contribute to an extension of the time during which a contact lens can be continuously worn by a wearer. High oxygen permeability is needed because the pupil of the eye has no blood circulation and extracts the oxygen needed by its cells directly from the atmosphere. Wettability is essential for wearer comfort. Resistance to protein and mucus deposits from fluids that bathe the outer surface of the eye is essential since without this feature the lens pores become clogged and both visual acuity and the oxygen permeability of the lens suffer.

20 Many types of contact lens compositions have been proposed. There are two general categories of contact lenses--rigid and hydrogel. For example, U.S. Patent Nos. 3,808,178 and 4,120,570 to Gaylord; 4,139,692 to Tanaka et al; 4,686,276 to Ellis et al;

4,743,106 to Novicky et al, and 4,812,598 to Chen propose the use of various copolymer compositions including silicon in contact lenses. The lenses are reasonably permeable to oxygen but are not of hydrogel or "soft" construction.

U.S. Patent No. 4,130,706 to Plambeck, Jr. proposes a methacrylate-type fluoropolymer ("FMA") for making contact lenses. While the lenses are described as hydrophilic and oxygen permeable, it is believed that they are not wettable enough to be truly comfortable to persons wearing the lenses and are not sufficiently permeable to oxygen to be worn safely and continuously for extended periods.

U.S. Patent No. 3,940,207 to Barkdoll proposes contact lenses constructed of fluorine-containing polymers that are soft and have a low refractive index. It is believed that these contact lenses are not sufficiently oxygen permeable to be worn safely for extended periods.

U.S. Patent Nos. 4,954,587 and 5,011,275 to Mueller propose soft, extended wear contact lenses based on N,N-dimethylacrylamide ("DMA"). While the lenses have a high oxygen permeability, the use of higher amounts of the relatively soft polymer of N,N-dimethylacrylamide is limited in that the lenses could become too soft to be fabricated.

It would be highly desirable to provide a hydrogel copolymer which can be used to form an easily fabricated pliable contact lens having the combination of oxygen permeability, wettability and resistance to protein and mucus deposits.

Summary of the invention

The present invention relates to a hydrogel copolymer for making contact lenses, the copolymer comprising, by weight, about 10 percent to about 85 percent of α -methylene-N-methylpyrrolidone or glycerdyl

methacrylate and mixtures thereof, from about 5 to about 25 percent of N,N-dimethylacrylamide, about 5 percent to about 80 percent of a polymerizable fluoromonomer, and about 1 percent to about 15 percent of a polymerizable hydrophobic, non-hydrolyzable silicone monomer. Optionally, an initiator and a crosslinker are employed under circumstances disclosed below.

In one embodiment of the invention, the copolymer comprises, by weight, from about 10 to 85 percent α -methylene-N-methylpyrrolidone, from about 5 to about 85 percent of glycerdyl methacrylate, from about 5 to about 60 percent of a polymerizable fluoromonomer, and from about 1 to about 15 percent of a polymerizable hydrophobic non-hydrolyzable silicone monomer.

In another embodiment, the copolymer comprises, by weight, from about 40 to about 90 percent of α -methylene-N-methylpyrrolidone and from about 10 to about 60 percent of a polymerizable fluoromonomer such as fluoroacrylates, styryl fluoromonomers and vinyl fluoromonomers.

Detailed Description of the Preferred Embodiments

The present invention will now be described more fully hereinafter. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiment set forth herein; rather, this embodiment is provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art.

The present invention utilizes in various combinations, as described below α -methylene-N-methylpyrrolidone (" α -MMP") or glycerdyl methacrylate ("GMA") and mixtures thereof, N,N-dimethyl methacrylamide, a polymerizable fluoromonomer, a

-4-

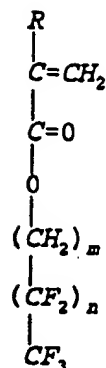
polymerizable hydrophobic, non-hydrolyzable silicone monomer, an initiator, and a crosslinker.

Preferably, the hydrogel copolymer comprises, by weight, from about 5 to about 85 percent of α -methylene-N-methylpyrrolidone or glycerdyl methacrylate and mixtures thereof, from about 10 to about 25 percent, and preferably from about 5 to about 20 percent of N,N-dimethylacrylamide, from about 5 to about 85 percent, and preferably from about 20 to about 40 percent by weight of a polymerizable fluoromonomer and from about 1 to about 15 percent, and preferably from about 2 to about 4 percent of a polymerizable hydrophobic non-hydrolyzable silicone monomer. Preferably, from about 20 to about 30 percent of α -methylene-N-methylpyrrolidone or from about 5 to about 30 percent of glycerdyl methacrylate is used. If a mixture of α -methylene-N-pyrrolidone and glyceridyl methacrylate is used, preferably from about 10 to about 85 percent of α -methylene-N-pyrrolidone and from about 5 to about 85 percent of glycerdyl methacrylate are used.

In one embodiment of the invention, from about 50 to about 90 percent of α -methylene-N-pyrrolidone can be blended with from about 10 to about 50 percent of a polymerizable fluoromonomer to form the hydrogel copolymer. In this embodiment, the hydrogel copolymer can further include, by weight, from about 10 to about 25 percent of a polymerizable hydrophilic monomer selected from the group consisting of methacrylic acid ("MA"), 2-hydroxyethylmethacrylate ("HEMA"), N-vinyl-2-pyrrolidone ("NVP") and N,N-dimethylacrylamide ("DMA").

The polymerizable fluoromonomer useful herein can vary. An exemplary fluoromonomer is one based on a fluoroacrylate composition which includes the following fluorine-containing monomer:

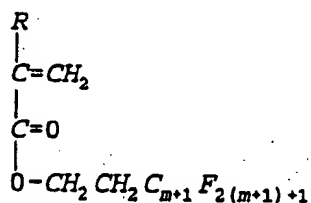
-5-



where R is H or CH₃, m is an integer from 0 to 9, and n is an integer from 1 to 4. A similar monomer is disclosed in U.S. Patent No. 4,130,706 to Plambeck, Jr., the disclosure of which is incorporated herein by reference.

5

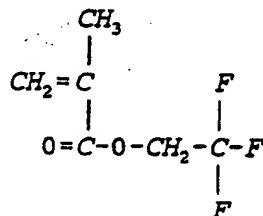
Another exemplary fluoromonomer can be a fluoracrylate



where R and m are defined as above. A similar monomer is disclosed in U.S. Patent No. 3,282,905 to Fosick et al, the disclosure of which is incorporated herein by reference.

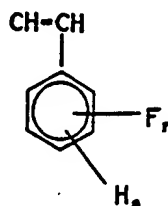
10

A particularly preferred composition is 2,2,2-trifluoroethyl methacrylate ("FMA").



-6-

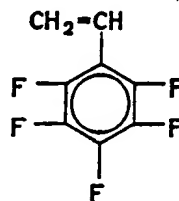
Alternatively, styryl fluoromonomers can be employed. The general formula of these monomers is



where $r + s = 5$ and $r = 1$ to 5 and $s = 5$ to 1.

A particularly preferred styryl fluoromonomer is pentafluorostyrene.

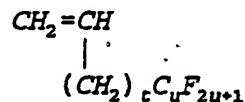
5



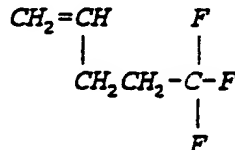
Other examples of fluoromonomers are p-vinyl benzyl trifluoroacetate and p-vinyl benzyl hexafluoroisopropyl ether.

Alternatively, vinyl fluoromonomers can be used. They have the general formula

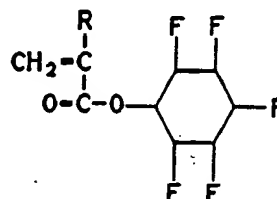
10



where $t = 1$ to 4 and $u = 1$ to 9. A particularly preferred vinyl fluoromonomer is 3,3,3-trifluorovinylpropane

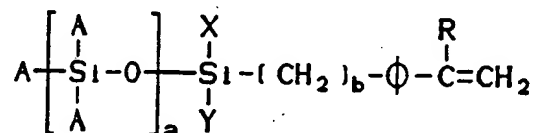


Alternatively, perfluorocyclohexyl acrylates can be used having the general formula

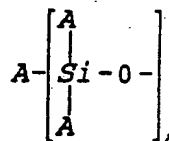


where R = H or CH₃. A particularly preferred pefluorocyclohexyl acrylate is perfluorocyclopentene. It is noted that only α-methylene-N-methylpyrrolidone and the polymerizable fluoromonomer can be used.

The polymerizable hydrophobic non-hydrolyzable silicone monomer useful herein can vary. An exemplary silicone has the formula



- where a is an integer from 1 to 5 and b is an integer from 0 to 6, A is selected from the group consisting of C₁-C₃ alkyl groups and phenyl groups, R is selected from the group consisting of a methyl group (CH₃) and hydrogen, X and Y are selected from the group consisting of C₁ to C₃ alkyl groups, phenyl groups and Z groups wherein Z is a group of the structure



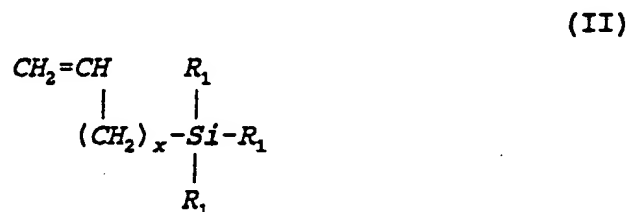
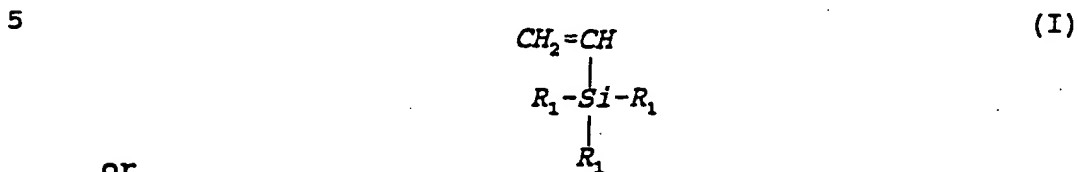
where a and A are as defined previously, and φ is a phenyl group. In the alkanol ester co-monomers, the alkyl group contains from 1 to 20 carbon atoms.

- Exemplary silicon-containing monomers are disclosed in U.S. Patent Nos. 3,808,178 and 4,120,570 to Gaylord,

-8-

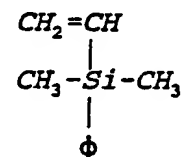
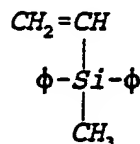
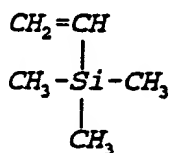
the disclosures of which are incorporated herein by reference.

Alternatively, vinyl silicone monomers can be employed. The general formula can be represented as



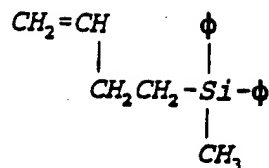
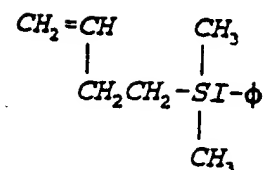
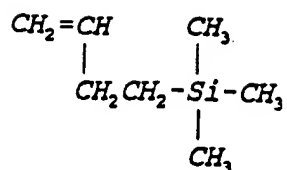
where X = 1 to 6 and R₁ is selected from the class consisting of C₁ to C₆ alkyl groups and phenyl groups or a mixture of alkyl and phenyl groups.

10 Particularly preferred examples of Class (I) are



where "φ" represents a phenyl group.

Particularly preferred examples of Class (II) are



In both classes of vinyl silicone monomers, any methyl group (CH_3 group) can be replaced by a benzene ring, as the preceding examples suggest.

5 Generally, vinyl silicone monomers are less reactive than acrylate silicone monomers. When vinyl silicone monomers are used, cobalt-60 ("Co-60"), radiation may be used as a source of polymerization energy. Co-60 may optionally be used as a source of polymerization energy even when vinyl silicone monomers are not employed.

10 Exemplary non-hydrolyzable silicones include methyldi(trimethylsiloxy)silylpropylglycerol methacrylate, methyldi(trimethylsiloxy)silylpropylglycerolethyl methacrylate, m,p-styrylethyltrimethylsilane, m,p-styrylethyltris(trimethylsiloxy)silane, methylacryloxypropyltris(trimethylsiloxy)silane and 4-(3-trimethylsilylpropyl)benzylstyrene sulfonate.

20 Preferably a crosslinker is used. The crosslinker can constitute, by weight, about 0.01 percent to about 5 percent and more preferably about 0.5 percent to about 2 percent of the weight of the hydrogel copolymer. The crosslinker is preferably one of a mixture of ethyleneglycoldimethacrylate ("EGDMA"), a fluorine-containing compound, or a silicon-containing

-10-

compound such as 1,3-bis[(p-acryloxymethyl)phenethyl]tetramethyldisiloxane or bis(3-methacryloxypropyl)tetramethyldisiloxane.

5 A quantity of an initiator equal in weight to 0.05 percent to 2 about percent of the weight of the mixture of monomers is preferably added thereto, except when Co-60 is used as a source of polymerization energy. The initiator may be selected from the group consisting essentially of 2,2'-azobis(2,4-
10 dimethylvaleronitrile) ("VAZO 52"), azobisisobutyronitrile ("AIBN"), benzoinmethylether ("BME"), di(sec-butyl)peroxydicarbonate ("SBC"), and isopropylperoxydicarbonate ("Ipp"). The initiator may also be any of those disclosed in the U.S. Patent
15 No. 4,120,570, to Gaylord, i.e., acetyl peroxide, lauroyl peroxide, decanoyl peroxide, caprylyl peroxide, benzoyl peroxide, tertiary-butyl peroxyphthalate, diisopropyl peroxydicarbonate, tertiary-butyl peroctoate, and α,α' -azobisisobutyronitrile.

20 VAZO 52 or AIBN may be used as an initiator when polymerization is aided by ultraviolet or thermal radiation, BME may be used as the initiator when polymerization is aided by the ultraviolet radiation, and SBC or Ipp may be used as the initiator when
25 polymerization is aided by thermal radiation. Co-60 or another radioactive source may also be used to promote polymerization, particularly when vinyl silicone monomers or other monomers that are not highly reactive are employed. When Co-60 or another radioactive source
30 is not used, polymerization energy is supplied in the form of thermal energy or in the form of ultraviolet radiation, as may be appropriate in view of the initiator employed. When Co-60 radiation is employed, no initiators are needed.

35 After curing, the resulting polymer is formed in any conventional or otherwise suitable process into contact lenses. The lenses have a shore hardness (D

-11-

scale) within the range of 82 to 89. Oxygen permeability in DK units ($\text{ml cm/cm}^2 \text{ sec cmHg} \times 10^{-10}$) at 35°C is within the range of 20 to 55. The contact angle is within the range of 10°-34°, light transmission is greater than 95%, refractive index is close to that of HEMA, and the coefficient of expansion is within the range of 1.1 to 1.6.

The following examples set forth representative formulas for the materials used in making contact lenses according to the invention:

Example 1

The following are mixed at room temperature in a 100ml beaker:

	<u>Ingredients</u>	<u>Percent By Weight</u>
	α -MMP ¹	9.97
	FMA ²	34.89
	DMA ³	24.42
	MDC ⁴	29.91
20	EGDMA ⁵ (crosslinker)	.49
	Ipp ⁶ (initiator)	0.03

The initiator is added to the mixture, and the mixture is poured into a test tube and polymerized by thermal polymerization (i.e., application of heat) at a temperature of 30°C for approximately 10 hours.

¹ α -methylene-N-methylpyrrolidone

² 2,2,2-trifluoroethylmethacrylate available from Aldrich Chemical Company of Milwaukee, Wisconsin

³ N,N-dimethylacrylamide available from Aldrich Chemical Company

30 ⁴ methylacryloxypropyltris(trimethylsiloxy)silane available from Huls America, Inc. of Newark, New Jersey

⁵ ethyleneglycoldimethacrylate available from Rohm Tech, Inc. of Marden, Massachusetts

⁶ isopropylperoxydicarbonate available from Polyscience, Inc. of Warrington, Pennsylvania

-12-

This is accomplished by placing the test tube in a hot water bath at a temperature of 30°C. The polymerized material is a colorless, solid, transparent polymer. The polymer is lathe-cut into buttons of conventional shape and size. The buttons are ground to the shape of contact lenses having respective center thicknesses of 0.1mm to 0.2mm, and then polished. The lenses are highly transparent (light transmission is greater than 95%) and have uniform optical properties. They have an oxygen permeability of 35 DK units at 35°C (normal eye temperature), a contact angle of less than 18°, and a refractive index of 1.405.

The following examples are similar to Example 1 but illustrate variations of the materials and quantities thereof employed and of the method of polymerization.

Example 2

	<u>Ingredients</u>	<u>Percent By Weight</u>
	α -MMP	9.97
20	FMA	19.94
	DMA	39.38
	MDC	29.90
	EGDMA	.50
	BME ⁷	0.02
25	The mixture is molded in the form of shells and polymerized by ultraviolet radiation in accordance with U. S. Patent No. 4,812,598 to Chen, the disclosure of which is incorporated herein by reference. The shells are lathe-cut to form contact lenses in accordance therewith.	
30		

⁷benzoinmethylether initiator available from Polyscience, Inc.

-13-

Example 3

5	<u>Ingredients</u>	<u>Percent By Weight</u>
	α -MMP	64.74
	MDC	9.96
	FMA	24.90
	BME	0.04

10 The mixture is molded in the form of shells and polymerized by UV polymerization in accordance with Example 2. The shells are lathe-cut to form contact lenses in accordance therewith.

Example 4

15	<u>Ingredients</u>	<u>Percent By Weight</u>
	α -MMP	10.00
	FMA	30.00
	DMA	29.50
20	MDC	30.00
	EDGMA	0.50
	BME	0.02

25 The mixture is molded in the form of shells and polymerized by UV polymerization in accordance with Example 2. The shells are lathe-cut to form contact lenses in accordance therewith.

Example 5

30	<u>Ingredients</u>	<u>Percent By Weight</u>
	GMA	10.00
	MDC	11.40
	FMA	25.00
	DMA	53.50
	EGDMA	0.10
35	VAZO-52	0.20

-14-

The mixture is molded in the form of shells and polymerized by thermal polymerization in accordance with Example 1. The shells are lathe-cut to form contact lenses in accordance therewith.

5 The lenses are highly transparent (light transmission is greater than 95%) and have uniform optical properties. They have an oxygen permeability of 46.7 DK units at 35°C (normal eye temperature), an expansion factor of 1.39, and a water content of about
10 54 percent.

Example 6

	Ingredients	Percent By Weight
	α -MMP	57.95
15	NVP ⁸	20.00
	FMA	15.00
	MDC	7.00
	EGDMA	0.05
	VAZO-52	0.02

20 The mixture is molded in the form of shells and polymerized by UV polymerization in accordance with Example 2. The shells are lathe-cut to form contact lenses in accordance therewith.

25 The lenses are highly transparent (light transmission is greater than 95%) and have uniform optical properties. They have an oxygen permeability of 47.4 DK units at 35°C, an expansion factor of 1.4, and a water content of about 65 percent.

⁸N-vinyl-2-pyrrolidone

-15-

Example 7

	<u>Ingredients</u>	<u>Percent By Weight</u>
	α -MMP	75.00
5	FMA	24.70
	EGDMA	0.30
	VAZO-52	0.30

10 The mixture is molded in the form of shells and polymerized by UV polymerization in accordance with Example 2. The shells are lathe-cut to form contact lenses in accordance therewith.

15 The lenses are highly transparent (light transmission is greater than 95%) and have uniform optical properties. They have an oxygen permeability of 25 DK units at 35°C, an expansion factor of 1.32, and a water content of about 54.4 percent.

Example 8

	<u>Ingredients</u>	<u>Percent By Weight</u>
20	α -MMP	80.00
	FMA	19.20
	EGDMA	0.30
	BME	0.30

25 The mixture is molded in the form of shells and polymerized by UV polymerization in accordance with Example 2. The shells are lathe-cut to form contact lenses in accordance therewith.

30 The lenses are highly transparent (light transmission is greater than 95%) and have uniform optical properties. They have an oxygen permeability of 62.7 DK units at 35°C, an expansion factor of 1.69, and a water content of 77.3 percent.

Example 9

	<u>Ingredients</u>	<u>Percent By Weight</u>
	α -MMP	67.95
5	GMA	17.00
	FMA	10.00
	MDC	5.00
	EGDMA	0.05
	VAZO-52	0.02

10 The mixture is molded in the form of shells and polymerized by UV polymerization in accordance with Example 2. The shells are lathe-cut to form contact lenses in accordance therewith.

15 The lenses are highly transparent (light transmission is greater than 95%) and have uniform optical properties. They have an oxygen permeability of 45.5 DK units at 35°C, an expansion factor of 1.38, and a water content of 62.5 percent.

20 Thus there is provided in accordance with the invention a novel and highly-effective contact lens that has an exceptional combination of oxygen permeability, wettability and resistance to protein and mucus deposits. A novel material for manufacturing the lens is also provided, and it is noted that the
25 material may be used for other medical articles needing the combination of oxygen permeability, wettability and resistance to protein and mucus deposits.

30 Many modifications of the preferred embodiments of the invention disclosed above will readily occur to those skilled in the art upon consideration of this disclosure. For example, initiators other than the ones disclosed may be employed, the contact lens may be tinted or clear, the temperature and times of polymerization may vary, etc.
35 Accordingly, the invention is not limited except by the appended claims.

-17-

That Which Is Claimed Is

1. A hydrogel copolymer useful for making pliable contact lenses, said copolymer comprising, by weight:

- 5 (a) from about 5 to about 85 percent of α -methylene-N-methylpyrrolidone or glycerdyl methacrylate and mixtures thereof;
- (b) from about 5 to about 35 percent of N,N-dimethylacrylamide;
- 10 (c) from about 5 to about 60 percent of a polymerizable fluoromonomer; and
- (d) from about 1 to about 15 percent of a polymerizable hydrophobic non-hydrolyzable silicone monomer.

2. A hydrogel copolymer according to Claim 1 wherein the weight of the α -methylene-N-methylpyrrolidone is about 20 to about 30 percent by weight.

3. A hydrogel copolymer according to Claim 1 wherein the weight of the glycerdyl methacrylate is about 5 to about 30 percent by weight.

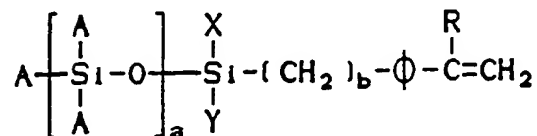
4. A hydrogel copolymer according to Claim 1 wherein the weight of said fluoromonomer is from about 20 percent to about 40 percent by weight.

5. A hydrogel copolymer according to Claim 1 wherein the weight of said silicone monomer is from about 2 percent to about 4 percent of the weight of said copolymer.

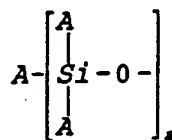
6. A hydrogel copolymer according to Claim 1 wherein said fluoromonomer is selected from the group consisting of fluoroacrylates, styryl fluoromonomers, and vinyl fluoromonomers.

-18-

7. A hydrogel copolymer according to Claim 1 wherein said silicone monomer is



where a is an integer from 1 to 5 and b is an integer from 0 to 6, A is selected from the group consisting of C₁-C₅ alkyl groups and phenyl groups, R is selected from the group consisting of a methyl group (CH₃) and hydrogen, X and Y are selected from the group consisting of C₁ to C₅ alkyl groups, phenyl groups and Z groups wherein Z is a group of the structure



where a and A are as defined previously, and ϕ is a phenyl group.

8. A hydrogel copolymer according to Claim 1 wherein said silicone monomer is selected from the group consisting of methyldi(trimethylsiloxy)silylpropylglycerol methacrylate, methyldi(trimethylsiloxy)silylpropylglycerolethyl methacrylate, m,p-styrylethyltrimethylsilane, m,p-styrylethyltris-(trimethylsiloxy)silane, methylacryloxypropyltris-(trimethylsiloxy)silane and 4-(3-trimethylsilylpropyl)-benzylstyrene sulfonate.

9. A hydrogel copolymer according to Claim 1 further comprising, by weight, about 0.01 to about 5 percent, of an initiator selected from the group consisting of 2,2'-azobis(2,4-dimethylvaleronitrile), azobisisobutyronitrile, benzoinmethylether, di(sec-butyl)peroxydicarbonate, and isopropylperoxydicarbonate.

10. A hydrogel copolymer according to Claim 1 further comprising, by weight, about 0.05 to about 2 percent of a crosslinker selected from the group consisting of a silicon-containing crosslinker, a fluorine-containing crosslinker, ethyleneglycoldimethacrylate and mixtures thereof.

11. A hydrogel copolymer useful for making pliable contact lenses, said copolymer comprising, by weight:

- (a) from about 10 to about 85 percent of α -methylene-N-methylpyrrolidone;
- (b) from about 5 to about 85 percent of glycerdyl methacrylate;
- (c) from about 5 to about 60 percent of a polymerizable fluoromonomer; and
- (d) from about 1 to about 15 percent of a polymerizable hydrophobic non-hydrolyzable silicone monomer.

12. A hydrogel copolymer according to Claim 11 wherein the weight of the α -methylene-N-methylpyrrolidone is about 20 to about 30 percent by weight.

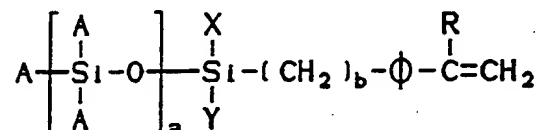
13. A hydrogel copolymer according to Claim 11 wherein the weight of the glycerdyl methacrylate is about 5 to about 30 percent by weight.

-20-

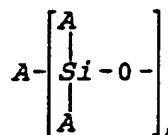
14. A hydrogel copolymer according to Claim 11 wherein the weight of said fluoromonomer is about 20 percent to about 40 percent of the weight of said copolymer.

15. A hydrogel copolymer according to Claim 11 wherein the weight of said silicone monomer is about 2 percent to about 4 percent of the weight of said copolymer.

16. A hydrogel copoloymer according to Claim 11 wherein said silicone monomer is



5 where a is an integer from 1 to 5 and b is an integer from 0 to 6, A is selected from the group consisting of C₁-C₅ alkyl groups and phenyl groups, R is selected from the group consisting of a methyl group (CH₃) and hydrogen, X and Y are selected from the group consisting of C₁ to C₅ alkyl groups, phenyl groups and Z groups wherein Z is a group of the structure



10

where a and A are as defined previously, and ϕ is a phenyl group.

-21-

17. A hydrogel copolymer according to Claim 11 wherein said silicone monomer is selected from the group consisting of methyldi(trimethylsiloxy)silylpropylglycerol methacrylate, methylidi(trimethylsiloxy)silylpropylglycerolethyl methacrylate, m,p-styrylethyltrimethylsilane, m,p-styrylethyltris(trimethylsiloxy)silane, methylacryloxypropyltris(trimethylsiloxy)silane and 4-(3-trimethylsilylpropyl)-benzylstyrene sulfonate.

18. A hydrogel copolymer according to Claim 11 further comprising, by weight, about 0.01 to about 5 percent, of an initiator selected from the group consisting of 2,2'-azobis(2,4-dimethylvaleronitrile), azobisisobutyronitrile, benzoinmethylether, di(sec-butyl)peroxydicarbonate, and isopropylperoxydicarbonate.

19. A hydrogel copolymer according to Claim 11 further comprising, by weight, about 0.05 to about 2 percent of a crosslinker selected from the group consisting of a silicon-containing crosslinker, a fluorine-containing crosslinker, ethyleneglycoldimethacrylate and mixtures thereof.

20. A hydrogel copolymer useful for making pliable contact lenses, said copolymer comprising, by weight:

(a) from about 40 to about 90 percent of α -methylene-N-methylpyrrolidone and

(b) from about 10 to about 60 percent of a polymerizable fluoromonomer selected from the group consisting of fluoroacrylates, styryl fluoromonomers and vinyl fluoromonomers.

-22-

21. A hydrogel copolymer according to Claim 20 further comprising, by weight:

5 (c) from about 1 to about 15 percent of a polymerizable hydrophobic non-hydrolyzable silicone monomer;

(d) from about 0.01 to about 5 percent of an initiator selected from the group consisting of claim 1 further comprising, by weight, about 0.01 to about 5 percent, of an
10 initiator selected from the group consisting of 2,2'-azobis(2,4-dimethylvalero- nitrile), azobisisobutyronitrile, benzoinmethylether, di(sec-butyl)peroxydicarbonate, and isopropylperoxydicarbonate; and

15 (e) from about 0.05 to about 2 percent of a crosslinker selected from the group consisting of claim 1 further comprising, by weight, 0.05 to about 2 percent of a crosslinker selected from the group
20 consisting of a silicon-containing crosslinker, a fluorine-containing crosslinker, and ethyleneglycol-dimethacrylate mixtures thereof.

22. A hydrogel copolymer according to Claim 20 or 21 further comprising, by weight, from about 10 to about 25 percent of a polymerizable hydrophilic monomer selected from the group consisting
5 of methacrylic acid, 2-hydroxyethylmethacrylate, N-vinyl-2-pyrrolidone and N,N-dimethylacrylamide.

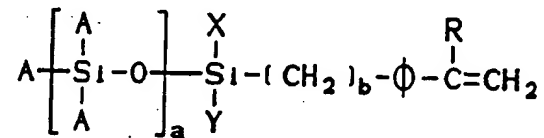
23. A hydrogel copolymer according to Claim 20 wherein the weight of the α -methylene-N-methylpyrrolidine is about 60 to about 80 percent by weight.

-23-

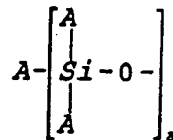
24. A hydrogel copolymer according to claim 20 wherein the weight of said fluoromonomer is about 20 percent to about 40 percent of the weight of said copolymer.

25. A hydrogel copolymer according to claim 20 wherein said styryl fluoromonomer is selected from the group consisting of pentafluorostyrene, p-vinyl benzyltrifluoroacetate and p-vinyl benzyl hexafluoroisopropylether.

26. A hydrogel copolymer according to claim 20 wherein said silicone monomer is



where a is an integer from 1 to 5 and b is an integer from 0 to 6, A is selected from the group consisting of C₁-C₅ alkyl groups and phenyl groups, R is selected from the group consisting of a methyl group (CH₃) and hydrogen, X and Y are selected from the group consisting of C₁ to C₅ alkyl groups, phenyl groups and Z groups wherein Z is a group of the structure



where a and A are as defined previously, and ϕ is a phenyl group.

-24-

27. A hydrogel copolymer according to Claim 20 wherein said silicone monomer is selected from the group consisting of methyldi(trimethylsiloxy)silylpropylglycerol methacrylate, methylidi(trimethylsiloxy)silylpropylglycerolethyl methacrylate, m,p-styrylethyltrimethylsilane, m,p-styrylethyltris-(trimethylsiloxy)silane, methylacryloxypropyltris-(trimethylsiloxy)silane and 4-(3-trimethylsilylpropyl)-benzylstyrene sulfonate.

28. A contact lens made from the hydrogel copolymer of Claims 1, 11 or 20.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/03128

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08F220/24; C08F226/06; G02B1/04

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

C08F ; G02B

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	GB,A,2 152 064 (TOYO CONTACT LENS) 31 July 1985 see page 2, line 28 - line 38 see page 3, line 13 - line 18 see claims 1-8 ---	1-28
Y	US,A,4 182 822 (CHANG) 8 January 1980 see claim 1 ---	1-28
A	FR,A,2 256 932 (UNION OPTICS CORPORATION) 1 August 1975 see the whole document ---	1, 3, 11, 13, 28
A	WO,A,9 104 283 (CHANG) 4 Apr 11 1991 see page 5, line 35 - page 6, line 27 see claims 1-3, 6, 7, 12, 13 ---	1, 3, 5, 7, 8, 11, 13, 15-17, 28

	-/-	

¹⁰ Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

¹¹ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention¹² document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step¹³ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.¹⁴ document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

11 SEPTEMBER 1992

Date of Mailing of this International Search Report

17. 09. 92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

ANDRIOLLO G. R.

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT

(CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 295 947 (OCULAR TECHNOLOGIES) 21 December 1988 see claims 1-13 ---	1,8,28
A	EP,A,0 253 515 (OPTIMERS COMPANY) 20 January 1988 see page 3, line 53 - page 6, line 42 ---	1,6,28

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9203128
SA 59913**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 11/09/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2152064	31-07-85	JP-B- 1015847	20-03-89
		JP-C- 1534024	12-12-89
		JP-A- 61034521	18-02-86
		AU-B- 558843	12-02-87
		AU-A- 3717684	04-07-85
		CA-A- 1223398	23-06-87
		DE-A, C 3446143	11-07-85
		FR-A, B 2557311	28-06-85
		US-A- 4547543	15-10-85

US-A-4182822	08-01-80	US-A- 4343927	10-08-82

FR-A-2256932	01-08-75	None	

WO-A-9104283	04-04-91	AU-A- 6331890	18-04-91
		CA-A- 2040419	15-03-91
		EP-A- 0443005	28-08-91
		JP-T- 4501882	02-04-92

EP-A-0295947	21-12-88	US-A- 4812598	14-03-89
		AU-A- 1812588	19-01-89
		JP-A- 1099021	17-04-89
		US-A- 4822864	18-04-89
		US-A- 4820747	11-04-89

EP-A-0253515	20-01-88	US-A- 4990582	05-02-91
		AU-A- 7577787	21-01-88
		JP-A- 63030820	09-02-88
		ZA-A- 8704762	05-01-88

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)